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(54) Title: SEDIMENTATION FREE JET INK COMPOSITION

(57) Abstract

Disclosed are ink compositions, particularly jet ink compositions that have low sedimentation rates comprising a carrier, a resin, and a pigment which is a nanostructured material. The pigment has a dry particle size of about 100 nm or less. Also disclosed is an improved process of jet printing on substrates, the improvement comprising projecting a stream of droplets of the jet ink composition to the surface of the substrate and controlling the direction of the stream so that the droplets are caused to form the desired printed message on the surface.

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SEDIMENTATION FREE JET INK COMPOSITION

The present invention generally relates to ink compositions, and particularly to an ink jet ink composition that is substantially free of sedimentation.

Printing ink compositions are known. Ink compositions generally contain a colorant which may be a dye, pigment, or lake dissolved or dispersed in a suitable medium such as a solvent or a dispersion medium. The quality of the printing ink and the success of the printing operation are to a great extent influenced by the quality of the colorant, particularly the pigment employed. This is especially important in ink compositions that are sensitive to operating parameters such as, for example, the ability to flow through fine orifices without interruption.

Ink jet printing is a well-known technique by which printing is accomplished without contact between the printing device and the substrate on which the printed characters are deposited. Briefly described, ink jet printing involves the technique of projecting a stream of ink droplets to a surface and controlling the direction of the stream so that the droplets are caused to form the desired printed image on that surface. The direction is controlled electronically in a continuous jet ink printing process, and by other means, e.g., pressure, in a drop-on-demand process. The technique of jet printing, which is a noncontact printing method, is well suited for application of characters onto a variety of surfaces including porous and non-porous surfaces including delicate surfaces such as food and pharmaceutical surfaces.

Reviews of various aspects of ink jet printing can be found in these publications: Kuhn et al., Scientific American, 162-178 (April 1979); and Keeling, Phys. Technol., 12(5), 196-303 (1981). Various ink jet

apparatuses are described, e.g., in the following U.S. patents: 3,060,429, 3,298,030, 3,373,437, 3,416,153, and 3,673,601.

In general, an ink jet ink composition must meet certain rigid requirements to be useful in ink jet printing operations. These relate to various parameters including viscosity, resistivity, solubility, compatibility of components, and wettability of the substrate. Further, the ink must be quick-drying and smear resistant, must be capable of passing through the ink jet nozzle without clogging, and must permit rapid cleanup of the printer components with minimum effort.

Ink jet inks have been formulated with colorants such as dyes, pigments, or combinations thereof. Pigments have been preferred because of the enhanced contrast, light stability, and durability obtainable by the use of pigments compared to that of soluble dyes. Enhanced solvent and/or water resistance of the printed message also has been observed with pigmented ink compositions.

Some pigmented inks heretobefore known have certain drawbacks. The pigments tend to settle with time. This restricts the manufacturers and suppliers from providing extended warranty on the ink and the printing operation. Agglomeration of the pigment and incompatibility of the pigment with the other ingredients of the ink are believed to be some of the causes for the settling phenomenon.

Attempts have been made to reduce or eliminate this settling problem. Resins and dispersing components have been included in the ink composition with the goal of maintaining the dispersion for prolonged periods of time. Further, to prevent agglomeration and settling, the ink is kept under agitation even when the jet printer is not in use. See, for example, U.S. Patent 4,365,035, which discusses this problem in some detail. The '035 patent discloses a jet ink composition containing a white pigment

such as titanium dioxide having a particle size of less than 5 µm. The '035 patent states that "some pigment settling will take place on prolonged storage" of the ink, and that "the action of pumping the ink through the system is sufficient to maintain the desired dispersion to within 95% of the original after more than 100 days of operation, while auxiliary stirring of the ink in the ink reservoir maintains the dispersion over an extended period of time", column 5, lines 1-9.

U.S. Patent 5,395,431 also highlights the importance of the need for an ink composition free of this problem. The '431 patent discloses a jet ink composition comprising a pigment such as carbon black and having a surface tension less than about 30 dynes/cm. To prepare this ink composition, the pigment is preferably pre-dispersed. The '431 patent states that the properties of the dispersion should remain constant at temperatures up to about 110°F, that the dispersion should not show any signs of sedimentation for at least 18 months, and that the sedimentation rate should remain less than 10 mg/hr. Column 3, lines 28-34.

The foregoing shows that there exists a need for ink compositions, particularly jet ink compositions, that are free or substantially free of sedimentation over extended periods of time. There further exists a need for ink compositions, particularly jet ink compositions, that are free or substantially free of pigment agglomeration.

The present invention provides an ink composition, particularly a jet ink composition, that is substantially free of sedimentation comprising an ink carrier, a resin, and a pigment which is a nanophase or nanostructured material. The jet ink composition of the present invention has a sedimentation rate of less than or about 1 mg/hr.

The pigment preferably has an average particle size of about 100 nm or less, and more preferably an average

particle size of about 50 nm or less, wherein the average particle size is determined on the dry pigment. When determined in the jet ink composition, the pigment preferably has an average particle size of about 300 nm or less, and more preferably an average particle size of from about 100 nm to about 250 nm.

The present invention further provides an improved process of jet printing on substrates, the improvement comprising projecting a stream of droplets of the inventive jet ink composition to the surface of the substrate and controlling the direction of the stream by a suitable means for controlling the direction so that the droplets are caused to form the desired printed message on the surface.

While the invention has been described and disclosed below in connection with certain preferred embodiments and procedures, it is not intended to limit the invention to those specific embodiments. Rather it is intended to cover all such alternative embodiments and modifications as fall within the spirit and scope of the invention.

The present invention provides ink compositions including jet ink compositions that are free or substantially free of sedimentation over extended periods of time. The ink compositions of the present invention preferably have a sedimentation rate of less than or about 1 mg/hr. The sedimentation rate of the ink composition can be determined by any suitable method, for example, by the use of a BYK-Chemie Dynometer Sedimentation Balance along with a strip chart recorder.

The jet ink composition of the present invention is suitable for printing onto porous and nonporous substrates including glass, metal, ceramic, paper, and plastics. The present invention provides a jet ink composition comprising a carrier, a resin, and a pigment which is a nanophase or nanostructured material. When used in a continuous ink jet

printing system, the jet ink composition has the following general properties: (1) a viscosity of from about 1.6 to about 10.0 centipoises (cps) at 25° C; and (2) an electrical resistivity of from about 50 to about 2000 ohm-cm. The continuous jet ink composition can have any suitable sonic velocity, preferably a sonic velocity of from about 1000 to about 2000 meters/second.

A detailed discussion of the ingredients and the characteristics of the inventive ink composition is set forth below.

INK CARRIER

Any suitable carrier can be used to prepare the ink compositions of the present invention. The carrier may be aqueous or non-aqueous. It is preferred, particularly for jet ink compositions, that the ink drying time is small so that printing can be accomplished rapidly and without smudging of the printed message.

If a nonaqueous carrier is used, typical carriers include lower aliphatic alcohols, ketones, esters, and ethers, and preferably lower aliphatic alcohols and lower ketones. Examples of preferred carriers include methanol, ethanol, acetone and methyl ethyl ketone. Examples of further preferred carriers include ethanol and acetone, and combinations thereof.

Any suitable amount of the carrier can be used. Typically, the carrier is present in an amount of from about 40% weight to about 80% by weight, and preferably from about 50% by weight to about 70% by weight of the ink composition.

COLORANT

The ink compositions of the present invention comprise one or more colorants, particularly pigments that impart the desired color to the printed message. Any suitable pigment can be used, and preferably a nanophase or nanostructured material is used. The nanophase material preferably has an average particle size of less than about 100 nm, more preferably below about 50 nm, wherein the average particle size is measured on the dry pigment. When measured on the ink composition, e.g., by the light scattering method, the pigment can have an average particle size of about 300 nm or less, and preferably an average particle size of from about 100 nm to about 250 nm.

The nanophase pigment can be an oxide, carbide, or nitride. Particular examples of pigments include titanium dioxide, titanium nitride, aluminum oxide, silicon dioxide, nickel oxide, gold oxide, zirconium dioxide, yttrium oxide (Y_2O_3), silicon carbide, silicon nitride (Si_3N_4), and ferric oxide.

The nanophase pigments can be obtained commercially or prepared by any suitable method known to those skilled in the art. Preferably, the pigments are prepared by the methods disclosed, e.g., in U.S. Patents 5,460,701, 4,642,207, and 5,128,081, and more preferably by the method disclosed in the '701 patent. Thus, for example, titanium metal can be vaporized into a plasma arc such as a tungsten inert gas plasma arc and the titanium vapor in the plasma can be reacted with a reaction gas such as oxygen to obtain TiO_2 nanocrystals. If the reaction gas is nitrogen instead of oxygen, titanium nitride nanocrystals result.

The nanocrystalline nanophase materials, especially those obtained by the plasma arc process, exhibit enhanced or unique properties compared to commonly available polycrystalline materials. The particle size of these nanocrystalline materials is highly uniform and the

particles agglomerate minimally compared to the polycrystalline materials such as the commonly available titanium dioxide and as disclosed, e.g., in U.S. Patent 4,365,035. The chemical stoichiometry of these nanocrystalline materials is also more easily controllable.

The nanocrystalline or nanophase materials have minimal agglomeration. The primary particles or single crystals tend to form smaller aggregates and the aggregates tend to form smaller agglomerates compared to commercially available common pigments. Thus, typical aggregate sizes are about 1 nm to about 50 nm and typical agglomerate sizes are about 10 nm to about 100 nm.

The particle sizes of these pigment particles can be measured on the dry pigment particles by transmission electron microscopy (TEM) or by the BET surface area measurement. TEM yields a visual inspection of the individual crystallites and BET infers an average particle size from a surface area measurement using the formula:

$$d = 6/pS,$$

wherein d is the mean particle diameter, p is the specific gravity (kg/m^3), and S is the measured specific surface area (m^2/g).

The particle sizes of particles in dispersions can be determined by the dynamic light scattering method which is known in the art.

Titanium dioxide nanocrystalline materials in powder form have an average BET particle size ranging from about 27 nm to about 84 nm and a density of 3.95 g/cc can be obtained from Nanophase Technologies Corp. in Burr Ridge, Illinois. The titanium dioxide is a mixture of 80% by weight anatase and 20% by weight rutile. The specific surface areas of these titanium dioxide materials and the average particle size are as follows: 18 m^2/g, 84 nm; 22 m^2/g, 69 nm; 41 m^2/g, 37 nm; 42 m^2/g, 36 nm; 48 m^2/g, 32 nm; and 57 m^2/g, 27 nm.

The pigments having small particle sizes, especially those having a particle size of about 100 nm or below, have high surface areas which provide at least one and possibly more than one of the following advantages in the ink printing technology. The pigment offers improved interaction with the surface modifiers to prevent agglomeration. Further, in combination with dyes, the pigments provide enhanced color strength and/or contrast. The pigment may offer improved adhesion of the printed message to substrates. The pigment also offers improved durability such as solvent and/or water resistance and light fastness to the printed message. These nanostructured pigments also can be combined with other pigments to obtain the desired color.

In addition to the pigments, the ink compositions of the present invention can also include a suitable dye. Examples of dyes include, but are not limited to, the yellow dyes such as C.I. Solvent Yellow 19 (C.I. 13900A), C.I. Solvent Yellow 21 (C.I. 18690), C.I. Solvent Yellow 61, C.I. Solvent Yellow 80, FD&C Yellow #5, Yellow Shade 16948, Acid Yellow 23, Levaderm Lemon Yellow (Mobay), Spirit Fast Yellow 3G, Aizen Spilon Yellow C-GNH (Hodagaya Chemical Co.), Yellow CGP (Ciba-Geigy), and the like, the orange dyes such as C.I. Solvent Orange 1 (C.I. 11920), C.I. Orange 37, C.I. Orange 40, Diaresin Orange K (Mitsubishi Chemical Industries, Ltd.), Diaresin Orange G (Mitsubishi Chemical Industries, Ltd.), Sumiplast Orange 3G (Sumitomo Chemical Co., Ltd.), and the like, red dyes such as C.I. Solvent Red 8, C.I. Solvent Red 81, C.I. Solvent Red 82, C.I. Solvent Red 84, C.I. Solvent Red 100, Cibacron Brilliant Red 38-A (Aldrich Chemical Co.), Drimarene Brilliant Red E-6A (Pylam, Inc.), Acid Red 92, Reactive red 31 (ICI America), and the like, pink dyes such as Diaresin Pink M (Mitsubishi Chemical Industries, Ltd.), Sumiplast Pink RFF (Sumitomo Chemical Co.), Direct Brill Pink B

Ground Crude (Crompton & Knowles), and the like, violet dyes such as C.I. Solvent Violet 8, C.I. Solvent Violet 21, Diaresin Violet (Mitsubishi), Diaresin Violet D, Sumiplast Violet RR (Sumitomo), and the like, blue dyes such as C.I. Solvent Blue 2, C.I. Solvent Blue 11, C.I. Solvent Blue 25, C.I. Solvent Blue 36, C.I. Solvent Blue 55, and the like, green dyes such as C.I. Solvent Green 3 and the like, brown dyes such as C.I. Solvent Brown 3 and Diaresin Brown A (Mitsubishi), and the like, black dyes such as C.I. Solvent Black 3, C.I. Solvent Black 5, C.I. Solvent Black 7, C.I. Solvent Black 22, C.I. Solvent Black 27, C.I. Solvent Black 29, Acid Black 123, and the like.

Any suitable amount of the colorant can be used. The colorant is generally present in the ink composition in an amount required to produce the desired contrast and readability. The colorant is preferably present in an amount of from about 0.1% to about 10% by weight, more preferably in an amount of from about 0.1% to about 5% by weight, and even more preferably in an amount of from about 0.1% to about 2% by weight of the ink composition.

RESIN

The ink composition of the present invention comprises at least one resin. The resin serves one or more useful functions in rendering an effective ink formulation. For example, it can act as a binder resin by forming a film on the pigment when the ink dries, thereby securing the colorant to the printed substrate. The film provides the printed messages a measure of protection against abrasion. The resin also can impart water and/or solvent resistance to the printed message.

The resin can also act as a surface modifier. Thus, the polar groups, such as for example, carboxy, hydroxy, amido, or amino groups present on the resin can facilitate interaction with the pigment, especially the polar sites on

the pigment, thereby providing a surface modified pigment which is more easily dispersible in or compatible with the ink formulation. The resin also can act as a cohesive force to hold together the contents of an ink drop, such as a jet ink drop.

Any suitable resin can be used, particularly resins having polar groups. Any known polar group can be present, for example, acidic, hydroxy, and basic groups. Further examples include carboxy groups and amino groups which can be primary, secondary, or tertiary.

The resin can have any suitable molecular weight. In general, the ability to form a durable film increases with an increase in molecular weight. Thus, the molecular weight of the resin can be as high as desired. An excessively high molecular weight may adversely affect the resin solubility or the viscosity of the ink composition. The weight average molecular weight of the resin can be in the range from about 1,500 to about 1,000,000, preferably in the range from about 5,000 to about 100,000, and more preferably in the range of from about 10,000 to about 50,000.

The resin can have any suitable acid, hydroxyl, or base number. An excessively high acid, hydroxyl, or base number can adversely affect the water resistance or solvent resistance. A very low acid, hydroxyl, or base number may not provide the desired solubility or dispersibility or the desired stabilization of the pigment particles. The acid, hydroxyl, or base number of the resin is typically in the range of from about 20 to about 500, preferably in the range of from about 50 to about 300, and more preferably in the range from about 200 to about 300. The acid, hydroxyl, and base numbers can be determined by the ASTM Method D 2849-69 (Reapproved 1980).

Typically, such resins include organic resins as commonly used in ink compositions, particularly ink jet ink

compositions, and include, for example, acrylic_copolymers, silicone resins, rosin esters, polyvinyl esters, ketone resins, urea aldehyde resins, vinyl chloride/vinyl ether or vinyl acetate copolymers, polyamide resins, styrene/maleate resins, polyvinylpyrrolidone resins, vinyl pyrrolidone/vinyl acetate copolymers, polystyrene resins, melamine resins, thermosetting acrylic resins, polyurethane resins and radiation curable acrylate resins.

Particular examples of resins containing acid groups include acrylic acid resins. These can be be obtained from S.C. Johnson & Co. in Racine, Wisconsin, which sells the acrylics under the tradename of JONCRYL. Examples of JONCRYL acrylics are the JONCRYL 555, 586, 678, 680, 690, 682, 683, and 67, which are water solubilized copolymers comprising styrene and acrylic acid. JONCRYL 690, a preferred resin for use in the jet ink composition of the present invention, has an average molecular weight of 15,500, an acid number of 240, a density of 1.07 g/cc, and a glass transition temperature of 102°C.

Another example of a suitable acrylic resin is the resin produced from at least one monomer selected from the group consisting of methyl, ethyl, butyl, and 2-ethylhexyl esters of (meth)acrylic acids and at least one monomer having a pendant amino group. The monomer having the amino group can be in an amount of from about 20% by weight to about 40% by weight of the resin. A particular example of such an acrylic resin is a copolymer of methyl methacrylate and 2-(dimethylamino)ethyl methacrylate, wherein the molar ratio of methyl methacrylate to 2-(dimethylamino)ethyl methacrylate is about 3.65. This copolymer can be prepared by free radical polymerization using an initiator such as AIBN, as described in U.S. Patent 4,834,799.

Any suitable silicone resin can be used, linear, branched or crosslinked, preferably those having a weight average molecular weight of from about 1000 to about

10,000, more preferably those having a weight average molecular weight of from about 2000 to about 8000, and even more preferably those having a weight average molecular weight of from about 2000 to about 4000. A particularly preferred silicone resin is the DOW CORNING™ 6-2230 resin.

A mixture or combination of the resins set forth above can also be employed.

The resin or a combination of resins can be present in the ink composition in a suitable amount. For example, the resin can be present in the jet ink composition in an amount of up to about 40% by weight of the composition, preferably in an amount of from about 1% by weight to about 20% by weight of the composition, and more preferably in an amount of from about 1% by weight to about 10% by weight of the ink composition.

ORGANIC SOLVENT

The ink compositions of the present invention can further include one or more organic solvents to increase the solubility or the dispersibility of the resin or the colorant, or to provide the desired viscosity. Any suitable organic solvent can be used. Examples of suitable classes of organic solvents include the polar solvents such as amides, esters, ketones, lactones, alcohols, and ethers. Examples of suitable organic solvents thus include methyl ethyl ketone, acetone, methanol, and ethanol. Some of the organic solvents, particularly the glycol ethers and N-methyl pyrrolidone, can act as humectants. It is known that humectants retard the drying rate of the ink at the print head.

Examples of glycol ethers include the mono- and di-alkyl ethers of alkylene glycols in which the alkyl group contains 1-6 carbon atoms (e.g., methyl, ethyl, propyl, butyl, etc.) and the alkylene glycol has 2-6 carbon atoms. Examples of suitable monoalkyl alkylene glycol ethers

include ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol butyl ether, ethylene glycol hexyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, diethylene glycol butyl ether, propylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, triethylene glycol ethyl ether, triethylene glycol methyl ether, and the like.

The organic solvent is preferably used in small amounts in view of environmental concerns. Further, an excessive amount of certain organic solvents can increase drying time of the printed message. For example, in a jet ink composition, particularly in an aqueous jet ink composition, the organic solvent is typically used in an amount that is below about 20% by weight of the ink composition, preferably in an amount of from about 0.1% by weight to about 10% by weight of the ink composition, and more preferably in an amount of from about 1% weight to about 5% by weight of the ink composition. When the organic solvent is used as a humectant, the humectant preferably is used in an amount of from about 0.5% by weight to about 5% by weight of the jet ink composition, and more preferably in an amount of from about 1% by weight to about 3% by weight of the jet ink composition.

SURFACTANT

The ink compositions of the present invention may further contain a surfactant to improve the spreading of the ink on the substrate or to provide the desired ink drop size. Any suitable surfactant can be used. The surfactant may be anionic, cationic, nonionic, or amphoteric.

Examples of anionic surfactants are, but are not limited to, alkylbenzenesulfonates such as dodecylbenzenesulfonate, alkylnaphthylsulfonates such as butyl or nonylnaphthylsulfonate, dialkylsulfosuccinates such as diamylsulfosuccinate, alcohol sulfates such as

sodium laurylsulfate, and perfluorinated carboxylic acids such as perfluorodecanoic acid and perfluorododecanoic acid.

Nonionic surfactants include the esters of polyethylene glycol, fatty acid esters of glycerol, fatty acid esters of glycol, and the like, and fluorochemical surfactants such as FC 170C, FC 430, FC 431, FC 740, FC 120, FC 248, FC 352, FC 396, FC 807, and FC 824, which are available from 3M Co. FC 430 and FC 431 are fluoroaliphatic polymeric esters. Cationic surfactants include alkylamines, amine oxides, amine ethoxylates, alkyl hydroxyalkyl imidazolines, quaternary ammonium salts, and amphoteric surfactants include the alkylbetaines, the amidopropylbetaines, and the like.

The surfactant may be present in the ink composition in any suitable amount. For example, in a jet ink composition, it is typically present in an amount of from about 0.01% to about 1% by weight of the jet ink composition, preferably in an amount of from about 0.1% to about 0.5% by weight of the jet ink composition, and more preferably in an amount of from about 0.2% to about 0.4% by weight of the jet ink composition.

PLASTICIZER

The ink compositions of the present invention can further include a plasticizer. The plasticizer may impart certain flexibility to the resin film that forms on the pigment particles and the substrate and improve the durability of the printed messages. Any suitable plasticizer known to those skilled in the art can be used. A preferred plasticizer is Monsanto's Plasticizer 8, which is N-ethyl-(o,p)toluenesulfonamide, particularly for use in jet ink compositions.

Any suitable amount of the plasticizer can be used. For example, in a jet ink composition of the present

invention, the plasticizer can be present in an amount of from about 0.01% by weight to about 5% by weight of the jet ink composition, preferably in an amount of from about 0.1% by weight to about 1% by weight.

CONDUCTIVITY AGENT

Jet printing ink compositions, continuous jet ink compositions in particular, should have a low specific resistivity, such as within the range of about 50 ohm-cm to about 2000 ohm-cm. Aqueous jet ink compositions generally possess the required electrical resistivity due the presence of basic ingredients such as ammonium hydroxide used to neutralize the acidic binder resins. Organic solvent based jet ink compositions may require adjustment of the resistivity.

The desired conductivity or resistivity can be achieved by the inclusion of an ionizable material. Examples of such ionizable materials include ammonium, alkali, and alkaline earth metal compounds such as ammonium hydroxide, lithium nitrate, lithium chloride, lithium thiocyanate, lithium trifluoromethanesulfonate, sodium chloride, potassium chloride, potassium bromide, calcium chloride, and the like, dimethylamine hydrochloride, and hydroxylamine hydrochloride. Any suitable amount of the ionizable material can be used. Normally, an ionizable material content of up to about 2% provides the desired conductivity.

ADHESION PROMOTER

The ink compositions of the present invention may further include an adhesion promoter to further improve the adhesion of the printed message to the substrates, particularly the nonporous substrates such as metal, glass or plastics. Any suitable adhesion promoter can be utilized, particularly a bifunctional adhesion promoter.

Examples of adhesion promoters include organosilanes and organotitanates. Examples of organosilanes include trichlorosilane, vinyltrichlorosilane, methyltrichlorosilane, methyldichlorosilane, mimethyldichlorosilane, methylvinyldichlorosilane, hexamethyldisilizane, methyltriethoxysilane, methyltrimethoxysilane, vinyltriethoxysilane, vinyltrimethoxysilane, vinyl-*tris*(2-methoxyethoxysilane), vinyltriacetoxysilane, *gamma*-methacryloxypropyl-trimethoxysilane, *gamma*-methacryloxypropyl-*tris*-(2-methoxyethoxy)silane, *beta*-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, and *gamma*-glycidoxypropyltrimethoxysilane. The organosilanes can be obtained from common supply houses and from Union Carbide Co. in Danbury, Connecticut.

Examples of organotitanates include transition metal organates such as titanium organates, zirconium organates, hafnium organates, and the like. Commercially available organates include the titanium organates sold by DuPont Chemical Co. under the tradename of TYZOR™ titanates. Examples of TYZOR titanates include TYZOR TBT, which is titanium tetra-n-butoxide, TYZOR TPT, which is titanium tri-isopropoxide, TYZOR GBA, which is titanium diisopropoxide bis(2,4-pentanedionate), TYZOR LA, which is titanium ammonium lactate, and TYZOR AA, which is titanium acetylacetonate.

Any suitable amount of the adhesion promoter can be used. For example, in a jet ink composition, the adhesion promoter is used preferably in an amount of from about 0.1% by weight to about 5% by weight of the ink composition, and more preferably in an amount of from about 0.5% by weight to about 2% by weight of the ink composition.

DEFOAMER

The ink compositions of the present invention, particularly water based jet ink compositions, preferably comprise a defoamer to prevent foaming of the ink during its preparation, as well as during the printing operation. Any suitable defoamer known to those of ordinary skill in the art can be used, preferably those that are miscible with the ink carrier.

Suitable defoamers include silicone defoamers and acetylenic defoamers. Examples of commercially available defoamers include silicone defoamers, such as DC-150, which can be obtained from Dow Corning Co., and SILWET I-77, 720, 722, or 7002, which can be obtained from Union Carbide Co.

Examples of suitable acetylenic defoamers include the SURFYNOL™ brand defoamers which can be obtained from Air Products and Chemical Co. in Allentown, Pennsylvania. A number of SURFYNOL defoamers are available, including the preferred SURFYNOL 104 (2,4,7,9-tetramethyl-5-decyn-4,7-diol), which is available as a solution in a variety of solvents as SURFYNOL 104A, SURFYNOL 104E, SURFYNOL 104H, and SURFYNOL 104BC, and other SURFYNOLs such as SURFYNOL GA, SURFYNOL SE, SURFYNOL TG, SURFYNOL PC, the dimethyl hexynediol, SURFYNOL 61, the dimethyl octynediol, SURFYNOL 82, the ethoxylated derivatives of the tetramethyl decynediol, SURFYNOL 440, SURFYNOL 465, and SURFYNOL 485.

Any suitable amount of the defoamer effective to prevent foaming of the ink during preparation and use can be used. The amount used is preferably in the range of from about 0.01% by weight to about 1% by weight of the ink composition, and more preferably in the range of from about 0.05% by weight to about 0.35% by weight of the ink composition. The weight percentages given above refer to that of the active ingredient, and if the defoamer is sold in a diluted form, the amount of the diluted defoamer used will be proportionately increased. Excessive use of the defoamers is to be avoided because it may adversely affect

the print quality such as the adhesion of the printed message to the substrate.

VISCOSITY

The jet ink compositions of the present invention, particularly the continuous jet ink compositions, have a viscosity within the range of about 1.0 to about 10 cps, and preferably about 1.0 to about 7.0 cps, as measured at 25°C, in order to achieve the desired rheological and performance characteristics. The viscosity of the ink composition of the invention can be conveniently regulated, as known to those of ordinary skill in the art, for instance, by suitable choice of the quantity and the molecular weight of the resin, the organic solvent, or other additives.

The ink compositions of the present invention can be prepared by any method known to those skilled in the art. Thus, for example, the resin is dissolved in a suitable amount of the solvent, and the pigment is then added and stirred at high speeds for a suitable time, e.g., about an hour. An adhesion promoter, such as a bifunctional silane, if needed, can be added and stirred. A defoamer is then added if necessary, followed by the addition of a conductivity enhancing agent, and a humectant, and mixed until a smooth ink composition is obtained.

In another method of preparing the ink composition, the resin can be melt mixed with a suitable oil, such as an oil that can be removed by vacuum, and the pigment is then added and mixed to obtain a melt containing the resin, the pigment, and the oil. The oil can then be removed by evaporation in vacuum. The melt is then mixed with suitable ink carrier and other necessary ingredients to obtain a ink composition.

The ink compositions of the present invention include all ink compositions wherein the use of the pigments as discussed above reduces the sedimentation or agglomeration, including ink compositions such as laminating inks as disclosed, e.g., in U.S. patent 4,895,888; in solvent or aqueous flexo/gravure inks, as disclosed e.g., in European patent application EP 0359 129 U.K. patent application GB 2 238 792 and U.S. Patents e.g., 4,690,712, 4,177,076 and 4,820,765; in printing inks such as disclosed in U.S. Patents 5,158,606 and 5,389,130; in lithographic printing inks such as disclosed in U.S. Patent 4,981,517, and in jet inks as disclosed, e.g., in U.S. Patent 5,316,575. For additional details on various types of inks, see e.g., Guthrie and Lin, "Physical-Chemical Aspects of Pigment Applications" in Surface Coating Reviews, J. T. Guthrie (Ed.), Oil & Colour Chemists' Association, Wembley, UK (1994). Hot-melt ink jet inks can also be prepared in accordance with the present invention.

The following examples further illustrate the present invention but, of course, should not be construed as in any way limiting its scope.

EXAMPLE 1

This Example illustrates the preparation of an embodiment of the inventive jet ink composition as well as the advantages of the inventive jet ink composition.

The following ingredients were combined and mixed until a smooth jet ink composition was obtained. The percentages of the ingredients listed below are by weight of the ink composition.

Ingredients	wt%
Acetone	53.5
Acrylic resin[1] (35% solution by wt. in MEK)	30.0
Titanium dioxide(Nanophase)[2]	10.0
Propyleneglycol monomethylether	4.0
10% FC-430 in 2-butanone (surfactant, 3M)	1.0
FC-122 (lithium trifluoromethanesulfonate)	1.0
Plasticizer 8 (Monsanto)	0.5
	100.0

[1]Copolymer of methyl methacrylate and 2-(dimethylamino)-ethyl methacrylate in a molar ratio of 3.65:1. [2]The dry pigment had a reported average particle size of 36 nm and a surface area of 42 m^2/g.

The average particle size of the pigment in the ink composition was measured by light scattering and was found to be 220 nm. The jet ink composition had a sedimentation rate of zero mg/hr based on a two-hour test. The jet ink composition was jet printed onto various substrates, including glass, metal, paper, and plastics, and satisfactory performance was obtained.

EXAMPLE 2

This Example illustrates the preparation of another embodiment of the inventive jet ink composition as well as the advantages of the inventive jet ink composition. The percentages of the ingredients listed below are by weight of the ink composition.

Ingredients	wt%
Acetone	69.7
JONCRYL 690 (S.C. Johnson)	12.0
Titanium dioxide(Nanophase)[1]	12.0
Propyleneglycol monomethyl ether	4.0
10% FC-430 in 2-butanone (surfactant, 3M)	0.8
FC-122 (lithium trifluoromethanesulfonate)	1.0
Plasticizer 8 (Monsanto)	0.5
	100.0

[1]The dry pigment had a reported average particle size of 69 nm and a surface area of 22 m^2/g.

The average particle size of the pigment in the ink composition was measured by light scattering and was found to be 231 nm. The jet ink composition had a sedimentation rate of zero mg/hr, based on a two-hour test. The jet ink composition was jet printed onto various substrates, including glass, metal, paper, and plastics, and satisfactory performance was obtained.

The present invention further provides an improved process of jet printing on substrates, the improvement comprising projecting a stream of droplets of the jet ink composition of the present invention to the surface of the substrate and controlling the direction of the stream so that the droplets are caused to form the desired printed message on the surface.

CLAIMS

1. A jet ink composition that is substantially free of sedimentation comprising an ink carrier, a resin, and a pigment which is a nanophase material.

2. A jet ink composition as claimed in claim 1, wherein said ink composition has a sedimentation rate of less than or about 1 mg/hr.

3. A jet ink composition as claimed in claim 1 or 2, wherein said pigment has an average particle size of 300 nm or less, said average particle size being determined in the jet ink composition.

4. A jet ink composition as claimed in claim 1 or 2, wherein said pigment has an average particle size of 100 nm or less, said average particle size being determined on the dry pigment.

5. A jet ink composition as claimed in claim 4, wherein said pigment has an average particle size of from 1 nm to 50 nm, said average particle size being determined on the dry pigment.

6. A jet ink composition as claimed in any one of the preceding claims, wherein said pigment is an oxide, carbide, or nitride.

7. A jet ink composition as claimed in claim 6, wherein said oxide is selected from the group consisting of titanium dioxide, nickel oxide, gold oxide, aluminum oxide, iron oxide, and combinations thereof.

8. A jet ink composition as claimed in any one of the preceding claims, wherein said ink carrier comprises an organic solvent.

9. A jet ink composition as claimed in claim 8, wherein said organic solvent is selected from the group consisting of acetone, 2-butanone, methanol, ethanol, and combinations thereof.

10. A jet ink composition as claimed in any one of the preceding claims, wherein said resin is an acrylic resin.

11. A jet ink composition as claimed in claim 10, wherein said acrylic resin has an amino group or a carboxyl group.

12. A jet ink composition as claimed in claim 11, wherein said acrylic resin is selected from the group consisting of a copolymer of methyl methacrylate and 2-(dimethylamino)ethyl methacrylate, a styrene-acrylic acid copolymer, and a combination thereof.

13. A jet ink composition as claimed in any one of the preceding claims, wherein said nanophase material is produced in a plasma arc system.

14. A jet ink composition as claimed in any one of the preceding claims, which further comprises a dye or a mixture of dyes.

15. In an improved process of jet printing on substrates, the improvement comprising projecting a stream of droplets of the jet ink composition as claimed in any one of the preceding claims to the surface of the substrate

and controlling the direction of the stream so that the droplets are caused to form the desired printed message on the surface.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/01352

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 622 429 A (CANON KK) 2 November 1994 see page 8, line 40 - line 43 see page 8, line 44 - page 9, line 6 see page 9, line 34 - line 40; example 2	1,3-8, 10,11,15
X	US 5 515 085 A (HOTOMI HIDEO ET AL) 7 May 1996 see column 5, line 1 - line 22 see column 5, line 35 - line 45 see column 5, line 61 - column 6, line 3	1,3, 6-11,15
X	US 5 538 548 A (YAMAZAKI HIDETO) 23 July 1996 see column 3, line 5 - line 20; table 1 see column 4, line 51 - column 5, line 22	1-5,8, 10,15

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 August 1998	20/08/1998

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 688 835 A (BROTHER IND LTD) 27 December 1995 see column 3, line 35 - column 4, line 12 see column 2, line 50 - line 58 see column 4, line 52 - column 5, line 25 see column 4, line 42 - line 46 ---	1,3-8, 10,15
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